REACTIONS OF OXYGEN TETRAFLUOROBORATE

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Introduction

Recently we developed an efficient method of preparing F_2O_2. This compound is known to react with boron trifluoride[1] to produce $O_2^+BF_4^-$. Little is known of the reaction of $O_2^+BF_4^-$ itself. It is relatively stable at room temperature, but reacts readily with organic compounds. For instance, tiny particles dropped into benzene or isopropyl alcohol instantly ignite fires. The only known inorganic reaction[1] is with NO_2 where oxygen is displaced giving $NO_2^+BF_4^-$. This paper describes some additional reactions of $O_2^+BF_4^-$ with inorganic as well as some organic compounds.

Results and Discussion

A. Inorganic Reactants

1. Xenon

Since xenon has nearly the same ionization potential as O_2, and since Xe^+ should be smaller than O_2^+, we felt that possibly xenon would replace oxygen to give the novel $Xe^+BF_4^-$. When liquid xenon (165°K) and solid $O_2^+BF_4^-$ ($Xe/O_2^+BF_4^- = 15$) were mixed in an evacuated tube, oxygen was released. The reaction was accomplished by allowing the xenon alternately to vaporize and condense around the $O_2^+BF_4^-$. After several minutes the sample was cooled in liquid nitrogen and any non-condensable gases were expanded into a fixed volume. The mass spectrum of the expanded gases showed only oxygen. The oxygen was pumped off; the reaction tube was warmed enough to liquefy the xenon and the procedure was repeated. This was continued until no further oxygen was obtained (about 85% of theory). Then the xenon was vaporized at 173°K (any BF_3 would also vaporize at this temperature) and expanded into a fixed volume. The loss of xenon (the amount reacted) was the same as the amount of oxygen collected. The mass spectrum indicated essentially no BF_3 was in the expanded xenon.

After removing all the xenon, the remaining white solid was slowly warmed. Decomposition became appreciable at 253°K with complete decomposition at room temperature. The mass spectrum of the gases showed Xe, BF_3, and F_2 with a $Xe:BF_3$ ratio of 1; we believe this to be evidence for the existence of $Xe^+BF_4^-$. Some O_2 was observed as well. The oxygen could have come from the decomposition of some unreacted $O_2^+BF_4^-$, or possibly from a xenon-oxygen compound of low stability. It is a firm conclusion that xenon reacts with $O_2^+BF_4^-$ at temperatures as low as 165°K to give free oxygen and a xenon compound.

2. Chlorine Dioxide

Chlorine dioxide was prepared by dropping sulfuric acid onto a mixture of $KClO_3$ and glass chips. The ClO_2 generated was then diluted in a stream of CO_2 and passed first through a drying tube (P_2O_5), then through a sample of

$O_2{}^+BF_4{}^-$ which was supported on a glass frit and cooled to 195°K. An immediate reaction occurred, releasing oxygen. Within minutes the reaction was completed. The product, a light-yellow solid, was unstable at room temperature. The mass spectrum of its decomposition products showed only m/q peaks for fragment ions from ClO_2, BF_3 and F_2. The product $ClO_2{}^+BF_4{}^-$ has previously been reported[2] from the reaction of chloryl fluoride with boron trifluoride.

3. Chlorine, Chlorine Trifluoride, and Ammonia

In hopes of preparing the novel $Cl_2{}^+BF_4{}^-$, $ClF_3{}^+BF_4{}^-$, and $NH_3{}^+BF_4{}^-$, we passed the corresponding gases through $O_2{}^+BF_4{}^-$. In each case oxygen was displaced. However, the products were not stable at the reaction temperature (223°K to 195°K).

4. Cyanogen

At 248°K, $O_2{}^+BF_4{}^-$ dissolved in liquid cyanogen to give a clear, colorless solution. However, no oxygen was displaced and $O_2{}^+BF_4{}^-$ was recovered after removal of the cyanogen.

B. Organic Reactants

Although benzene and isopropyl alcohol spontaneously inflame when a milligram of $O_2{}^+BF_4{}^-$ is added, we felt that reactions with other specific organic compounds (in particular perhalogenated materials) could be studied under carefully controlled conditions.

Indeed, when liquid CCl_4 was condensed around $O_2{}^+BF_4{}^-$ at 250°K, a smooth reaction occured to liberate O_2, Cl_2, and BF_3, forming $CFCl_3$ and CF_2Cl_2. In a like manner, $O_2{}^+BF_4{}^-$ reacted with CF_2Cl_2 at 233°K to form CF_3Cl, essentially quantitatively. No CF_4 was detected. Hexafluorobenzene also reacted with $O_2{}^+BF_4{}^-$ at 298°K to give O_2, F_2, BF_3, and fluorinated hydrocarbons with the following prominent ions in the mass spectrum: $CF_3{}^+$, $C_2F_4{}^+$, $C_2F_5{}^+$, and $C_3F_5{}^+$. Some oxygen was converted to CO_2 and COF_2. It was also found that methane and ethane will inflame at 195°K. However, there was no reaction between perfluorocyclobutane and $O_2{}^+BF_4{}^-$.

Of the compounds that were found to react readily with $O_2{}^+BF_4{}^-$, both methane and ClF_3 have higher ionization potentials than that of O_2 (12.2 ev). Cyanogen, with both unsaturation and a higher ionization potential, did not react. In the case of compounds with ionization potentials below or equal to that of O_2, a reasonable mechanism for reaction is electron transfer to liberate O_2 and form a new ion which may or may not react further.

It should be noted that no CF_4 was formed from the reaction of $O_2{}^+BF_4{}^-$ with CCl_2F_2, whereas CCl_2F_2 was a product from the reaction with CCl_4. This would be expected if the primary products from the unstable $CCl_2F_2{}^+BF_4{}^-$ and $CCl_4{}^+BF_4{}^-$ were $CClF_3$ and CCl_3F, respectively. The former product has a higher ionization potential (12.9 ev)[3][4] than O_2 and is less likely to react with $O_2{}^+BF_4{}^-$. Therefore no CF_4 was observed. On the other hand, CCl_3F has a favorable ionization potential, and further reaction with $O_2{}^+BF_4{}^-$ is possible, giving CCl_2F_2.

Acknowledgement

References

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